

Supplementary Material

Structure–Property Relationships Based on Phenyl-1*H*-Pyrrole End-Capped Thiophene Semiconductors

Ying Liu,^{A,B} Ji Zhang,^A Yunqi Liu,^{A,C} Gui Yu,^A Ziyi Ge^B

^ABeijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^BNingbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

^CCorresponding author. Email: liuyq@iccas.ac.cn

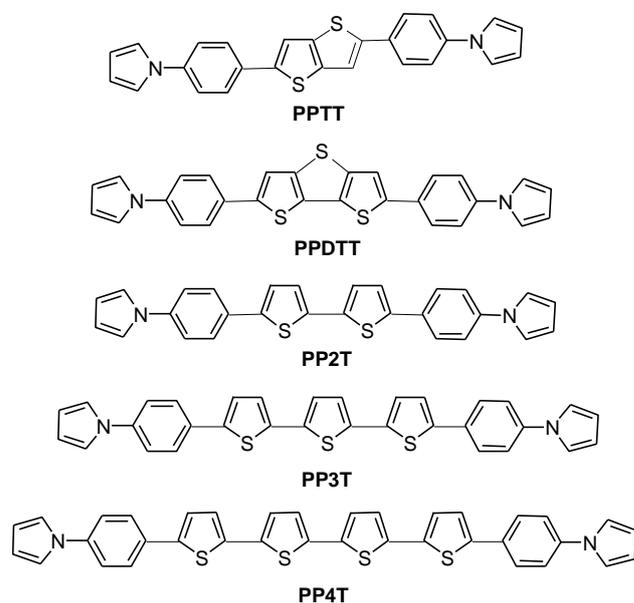


Figure A1. Structures of phenyl-1*H*-pyrrole end-capped thiophene oligomers.

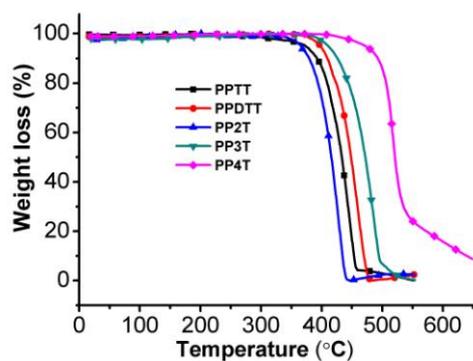


Figure A2. TGA plots.

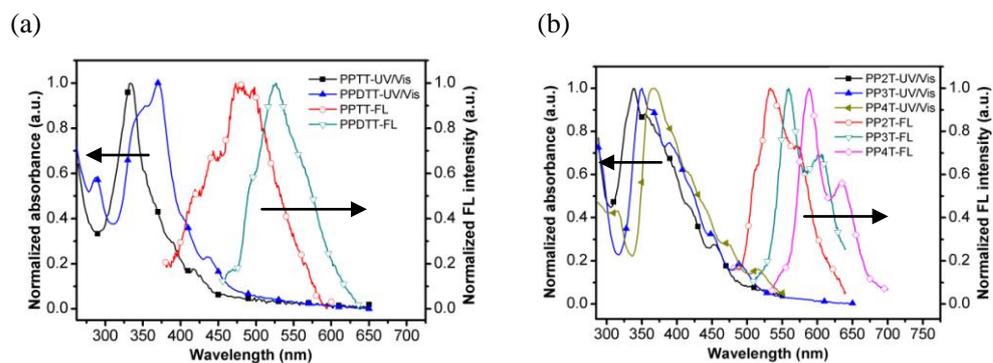


Figure A3. Optical properties of the target compounds deposited on quartz glass with a film thickness of ca. 50 nm.

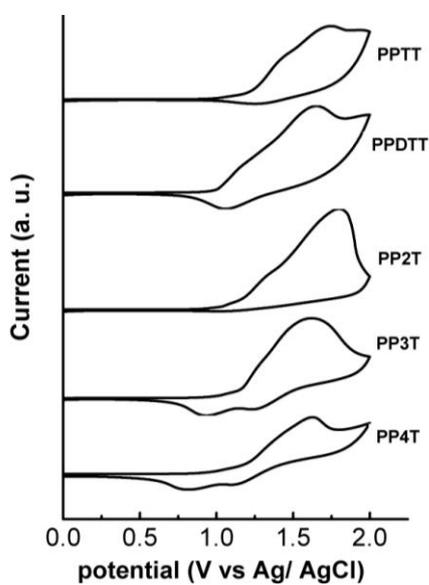


Figure A4. Cyclic voltammetry measured in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-THF}$.

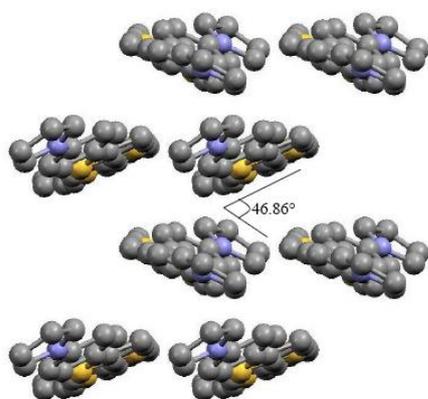


Figure A5. Stacking structure of **PP3T** with a view down the c axis (hydrogen atoms were omitted for clarity).

OFET Properties

The OFETs devices were made by sublimating the molecules (thickness: 50 nm) onto OTS-modified SiO₂/Si substrates, followed by Au deposition through a shadow mask to define the source and drain electrodes. Prior to the deposition, OTS was deposited by placing the SiO₂ substrates in a vacuum oven saturated with OTS vapour for 3 h. The performance were measured in a top contact configuration (drain and source electrodes deposited above the semiconductor). Gold source and drain contacts (50 nm) were deposited onto the organic layer through a shadow mask. The channel length (L) and width (W) were 50 and 3000 μm , respectively. The OFET characteristics of the devices were obtained at room temperature in air. The mobilities in the saturation regime were determined using the Equation 1

$$I_{\text{DS}} = (\mu_{\text{FET}}WC_i/2L)(V_{\text{G}} - V_{\text{T}})^2 \quad (1)$$

where I_{DS} is the drain-source current in the saturated regime, μ_{FET} is the field-effect mobility, W the channel width, L the channel length, C_i the capacitance SiO₂ dielectric layer, V_{G} the gate voltage and V_{T} the threshold voltage.

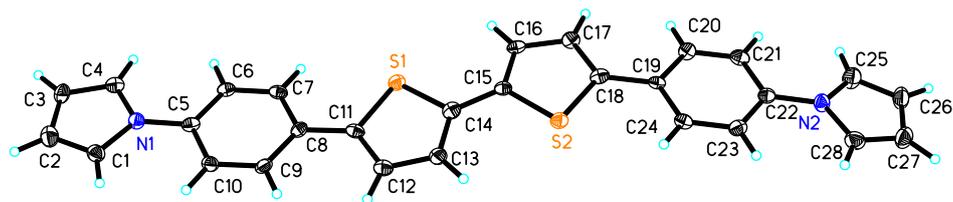
4.1. General Methods

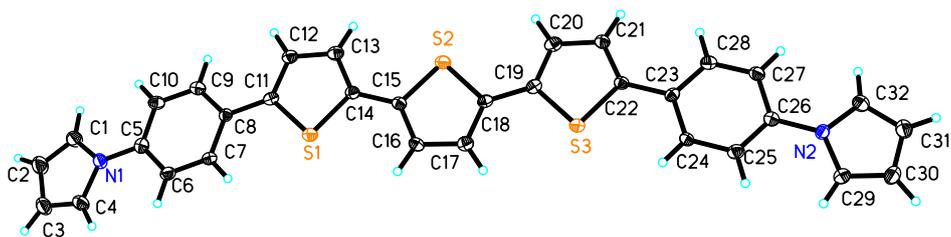
Elemental analysis was obtained on an Eager 300 elemental analyzer. NMR spectra were taken on a Bruker 300 MHz spectrometer. Chemical shifts of all compounds were reported relative to an internal tetramethylsilane (TMS) standard at 0.0 ppm. The thermo gravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermo gravimetric analyzer at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen flow. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC7 at a heating/cooling rate of 10/ -10 $^{\circ}\text{C min}^{-1}$ under nitrogen flow. UV-vis absorption spectra were obtained on a Perkin- Elmer Lambda 35 and Perkin-Elmer LS50B. The bandgaps were measured according to the onset absorption of UV-vis spectra ($E_{\text{g}} = 1240/\lambda_{\text{onset}}$ eV). Film cyclic voltammetry (CV) of the oligomers was performed on a CHI660a electrochemical analyzer with a three electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in acetonitrile at a scan rate of 80 mVs^{-1} . The thin films were prepared by vacuum deposition of the oligomers on a platinum plate electrode (0.6 cm^2). A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The potential was calibrated by the ferrocene/ferrocenium couple (0.42 V versus Ag/AgCl in acetonitrile). HOMO energies were estimated by the equation $E_{\text{HOMO}} = -(4.40 + E_{\text{onset}})$ (eV).^[11]

X-ray Diffraction Measurement: X-ray crystal structure measurements were carried out in the reflection mode using a Rigaku MM-007 X-ray diffraction system (Mo-K α radiation, $\lambda = 0.71073$ \AA). The data were collected at 173 K and the structure was solved by direct methods and SHELXS-97, and refined by using the SHELXL-97 program. Yellow platelet crystals of **PP3T** were obtained by slow sublimation by a temperature-gradient furnace. Crystallographic data for **PP3T**: Crystal size: 0.15 \times 0.15 \times 0.10 mm^3 ; Orthorhombic; P2₁2₁2₁; Z = 4; a = 5.7581 (5), b = 7.29990 (6), c = 57.115 (5) \AA ; V = 2400.4 (4) \AA^3 ; $\rho_{\text{calcd}} = 1.468$ g cm^{-3} ; final R = 0.0443, wR = 0.0722; GoF = 0.982 with I > 2.00 σ (I). CCDC-759957 (**PP2T**) and 759960 (**PP3T**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data collection and structure-refinement information of **PP2T** and **PP3T**.

	PP2T	PP3T
formula	C ₂₈ H ₂₀ N ₂ S ₂	C ₃₂ H ₂₂ N ₂ S ₃
formula weight	448.58	530.70
method of crystal growth	vacuum sublimation	vacuum sublimation
color and shape of crystal	yellow platelet	yellow platelet
crystal size (mm)	0.17 × 0.13 × 0.05	0.15 × 0.15 × 0.10
temperature (K)	173(2)	173(2)
crystal system	monoclinic	Orthorhombic
space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	5.761(3)	5.7581(5)
<i>b</i> [Å]	7.331(3)	7.2990(6)
<i>c</i> [Å]	24.6428(11)	57.115(5)
α [°]	90.00	90.00
β [°]	92.519(6)	90.00
γ [°]	90.00	90.00
<i>V</i> [Å ³]	1039.7(6)	2400.4(4)
<i>Z</i>	2	4
Calculated density ρ_{calcd} [g cm ⁻³]	1.433	1.468
Absorption coefficient, μ , (mm ⁻¹)	0.277	3.024
F(000)	468	1104
θ range [°]	2.90 ~ 25.00	3.10 ~ 68.25
index ranges	-6 ≤ <i>h</i> ≤ 5, -8 ≤ <i>k</i> ≤ 8, -29 ≤ <i>l</i> ≤ 29	-6 ≤ <i>h</i> ≤ 6, -8 ≤ <i>k</i> ≤ 8, -66 ≤ <i>l</i> ≤ 68
no. of reflections collected	6574	16647
completeness to θ [°]	25.00 (99.7 %)	68.25 (99.9 %)
absorption correction	Numerical	Numerical
max/min transmission	0.9863/0.9545	0.7519/0.6598
data/restraints/parameters	3618/1/290	4368/0/336
final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.0758, wR ₂ = 0.1426	R ₁ = 0.0443, wR ₂ = 0.0722
R indices (all data)	R ₁ = 0.0853 wR ₂ = 0.1489	R ₁ = 0.0599, wR ₂ = 0.0801
goodness of fit (GoF)	1.088	0.982
CCDC	759957	759960





4. Experimental Section

General.

Chemicals were purchased from Aldrich, Alfa Aesar and used as received. Solvents of tetrahydrofuran (THF), and toluene were distilled over sodium/benzophenone. All other chemical reagents and solvents were used as received from commercial sources without further purification. ^1H NMR (300 MHz) and ^1H NMR (400 MHz) spectra was obtained on a Bruker DMX-300 NMR and DMX-400 NMR Spectrometer using tetramethylsilane as internal standard. MS spectra were determined on Micromass GCT-MS spectrometer. Elemental analyses were performed on a Carlo Erba model 1160 elemental analyzer. Electronic absorption spectra were measured on a Jasco V570 UV–vis spectrophotometer. Emission spectra were recorded on Hitachi F-4500 fluorescence spectrometer. TGA measurements were carried out on a TA SDT 2960 instruments under a dry nitrogen flow, heating from room temperature (R.T.) to 550 °C, with a heating rate of 10 °C/min. DSC analyses were performed on a TA DSC 2010 instruments under a dry N_2 flow, heating from R. T. to 320 °C, at a heating rate of 10 °C/min. Cyclic voltammetric measurements were carried out on a computer-controlled CHI660C instruments at R.T. X-ray diffraction measurements were carried out in the reflection mode at R.T. using a 2-kW Rigaku X-ray diffraction system. X-ray diffraction (XRD) measurements were carried out in the reflection mode at R.T. using a Rigaku MM-007 X-ray diffraction system (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The films were imaged in air using a Digital Instruments Nanoscope III atomic force microscope operated in tapping mode. The OFET characteristics of the devices were obtained at room temperature in air by using a Hewlett–Packard (HP) 4140B semiconductor parameter analyzer.

4.5. Materials

2,5-dibromo-thieno[3,2-*b*]thiophene,^[2] 2,6-dibromo-dithieno[3,2-*b*;2',3'-*d*]thiophene^[3] were synthesized according to the reported methods. 2,2'-bithiophene, 2,2':5',2''-terthiophene, 2,2';5',2'';5'',2'''-quaterthiophene were purchased from Aldrich, Alfa Aesar and used as received. The same methodology was implemented for the synthesis of the three dibromo-thiophene compounds by two equiv of N-bromosuccinimide (NBS) in CHCl_3 .

Synthesis.

1-(4-Bromo-phenyl)-1*H*-pyrrole (1)

To a round bottomed flask containing the nitrogen pyrrole (15 mmol, 1.00 g), 1-bromo-4-iodo-benzene (15 mmol, 4.25 g), CuI (0.75 mmol, 143 mg), $n\text{Bu}_4\text{NBr}$ (0.75 mmol, 240 mg) and NaOH (30 mmol, 1.2 g) under a N_2 atmosphere was added toluene (50 mL). The reaction mixture was vigorously refluxed for 22 h. On cooling to room temperature, saturated NH_4Cl solution (50 mL) was added and the organic layer was extracted with EtOAc ($3 \times 50 \text{ mL}$). The

combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, Petroleum ether) to afford a white solid. Yield: 3.15 g, 95 %. ¹H NMR (CDCl₃, 400 MHz) δ = 7.52 (d, 2H), 7.28 (d, 2H), 7.04 (s, 2H), 6.35 (s, 2H). MS (EI): *m/z* (M⁺) 221; Elemental analysis (%): Anal. Calcd. For C₁₀H₈BrN: C 54.08, H 3.63, N 6.31; found: C 54.74, H 3.72, N 5.90.

1-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-1H-pyrrole (2)

A 3.2 g (14.5 mmol) sample of 1-(4-Bromo-phenyl)-1H-pyrrole (**1**) in 150 mL of dry THF was treated dropwise with 6.4 mL (16.2 mmol) of 2.5 M *n*-butyllithium at -78 °C under argon. After the solution was stirred for 0.5 h and warmed to -40 °C, 3.0 g (16 mmol) of tributylstannyl chloride was added to the solution, and the new solution was warmed to room temperature. The solvent was removed by rotary evaporation after the solution was stirred for 8 h. The organic layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, Petroleum ether: EtOAc = 10:1) to afford a white solids. Yield: 2.0 g, 75 %. ¹H NMR (CDCl₃, 400 MHz): δ = 7.83–7.85 (d, 2H), 7.52–7.54 (d, 2H) 7.30 (s, 2H) 6.31 (s, 2H); ¹³CNMR (CDCl₃) δ_C 205.1(s), 142.8 (s), 136.3 (s), 118.7 (s), 110.8 (s), 83.7 (s), 28.5 (m), 24.4 (d). MS (EI): *m/z* (M⁺) 269; Elemental analysis (%): Anal. Calcd. For C₁₆H₂₀BNO₂: C 71.40, H 7.49, N 5.20; found: C 71.58, H 7.47, N 5.04.

2,5-Bis(1-*p*-phenyl-1H-pyrrole)-thieno[3,2-*b*]thiophene (PPTT)

To a solution of 2,5-dibromo-thieno[3,2-*b*]thiophene (1.48 g, 5 mmol) and **2** (2.62 g, 10.3 mmol) dissolved in THF (50 mL) was added an aqueous 2 M potassium carbonate (K₂CO₃) solution (50 mL). After the solution was bubbled with nitrogen for 30 min, tetrakis-(triphenylphosphine)palladium (0) (Pd(PPh₃)₄, 173 mg, 0.15 mmol) was added. The mixture was heated to reflux for 48 hours under a nitrogen atmosphere. On cooling to room temperature, the final products precipitated from the reaction mixture. The precipitation was filtered and washed with dilute acid (5% HCl, 100 ml), water (100 ml), methanol (100 ml), then with acetone three times (50 ml × 3), to remove the starting material as well as the mono-substituted by-product. Further purification was carried out by sublimation three times to afford a light-yellow solid. Yield: 1.47 g, 70 %.

HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₆H₁₈N₂S₂, 422.0911; found, 422.0916. Elemental analysis (%): Anal. Calcd. For C₂₆H₁₈N₂S₂: C 73.90, H 4.29, N 6.63; found: C 73.67, H 4.34, N 6.25.

2,6-Bis(1-*p*-phenyl-1H-pyrrole)-dithieno[3,2-*b*;2',3'-*d*]thiophene (PPDTT)

PPDTT was prepared according to the procedure used for PPTT and Suzuki coupling reaction between 5,5'-dibromo-dithieno[3,2-*b*;2',3'-*d*]thiophene and boronate ester **2**. PPDTT was isolated as a yellow solid. Yield: 1.60 g, 60 %. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₈H₁₈N₂S₃, 478.0632; found, 478.0637. Elemental analysis (%): Anal. Calcd. For C₂₈H₁₈N₂S₃: C 70.26, H 3.79, N 5.85; found: C 70.01, H 3.74, N 5.74.

5,5'-Bis(1-*p*-phenyl-1H-pyrrole)-2,2'-bithiophene (PP2T)

PP2T was prepared according to the procedure used for PPTT and Suzuki coupling reaction between 5,5'-dibromo-2,2'-bithiophene and boronate ester **2**. PP2T was isolated as a yellow solid. Yield: 1.68 g, 75 %. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₈H₂₀N₂S₂, 448.1068; found, 448.1073. Elemental analysis (%): Anal. Calcd. For C₂₈H₂₀N₂S₂: C 74.97, H 4.49, N 6.24; found:

C 74.94, H 4.53, N 6.26.

5,5''-Bis(1-p-phenyl-1H-pyrrole)-2,2':5',2''-terthiophene (PP3T)

PP3T was prepared according to the procedure used for **PPTT** and Suzuki coupling reaction between 5,5''-dibromo-2,2':5',2''-terthiophene and boronate ester **2**. **PP3T** was isolated as a brown solid. Yield: 1.72 g, 65 %. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{32}H_{22}N_2S_3$, 530.0945; found, 530.0950. Elemental analysis (%): Anal. Calcd. For $C_{32}H_{22}N_2S_3$: C 72.42, H 4.18, N 5.28; found: C 72.39, H 4.18, N 5.23.

5,5'''-Bis(1-p-Phenyl-1H-pyrrole)-2,2';5',2'';5'',2'''-quaterthiophene (PP4T)

PP4T was prepared according to the procedure used for **PPTT** and Suzuki coupling reaction between 5,5'''-dibromo-2,2';5',2'';5'',2'''-quaterthiophene^[4] and boronate ester **2**. **PP4T** was isolated as a red solid. Yield: 1.83 g, 60 %. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{36}H_{24}N_2S_4$, 612.0822; found, 612.0828. Elemental analysis (%): Anal. Calcd. For $C_{36}H_{24}N_2S_4$: C 70.55, H 3.95, N 4.57; found: C 70.31, H 3.98, N 4.59.

References:

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- [1] X. K. Gao, W. P. Wu, Y. Q. Liu, S. B. Jiao, W. F. Qiu, G. Yu, L. M. Wang, D. B. Zhu, *J. Mater. Chem.* **2007**, *17*, 736–743; b) J. L. Brédas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, *105*, 6555–6561.
- [2] S.-H. Jung, H. K. Kim, S.-H. Kim, Y. H. Kim, S. C. Jeoung, D. Kim, *Macromolecules* **2000**, *33*, 9277–9288; b) L. S. Fuller, B. Iddon, K. A. Smith, *J. Chem. Soc. Perkin Trans.* **1997**, *1*, 3465–3470.
- [3] F. Allared, J. Hellberg, T. Remonen, *Tetrahedron Lett.* **2002**, *43*, 1553–1554; b) J. Frey, A. D. Bond, A. B. Holmes, *Chem. Commun.* **2002**, 2424–2425.
- [4] Z. H. Li, M. S. Wong, Y. Tao, H. Fukutani, *Org. Lett.* **2007**, *9*, 3659–3662.